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Polyelectrolyte "Catalysis" on the Interionic Reactions between Similarly Charged Polyvalent Ions[‡]

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ABSTRACT: The influence of polyelectrolytes on the rate of the interionic reactions between similarly charged polyvalent ions was studied. As expected, the overall reaction between U^{4+} and Tl^{3+} was accelerated with an anionic polymer, i.e., sodium poly(ethylene sulfonate), at most by a factor of 10^4 accompanied by an increase in the entropy of activation and in the volume of activation. The results indicated that the activated complex was dehydrated by the macroions to a much larger extent than the reactants. Of the two reaction pathways, it was found that the route via a hexavalent intermediate was accelerated by the anionic macroions to a larger extent than that via a pentavalent one, indicating that the stabilization of the activated complex was important in polyelectrolyte catalysis. The reaction between $Fe(CN)_6^{4-}$ and $S_2O_8^{2-}$ was accelerated by a factor of about 10^5 by cationic polymers, i.e., polybrene and poly(4-vinyl-*N*-ethylpyridinium bromide). The entropy and volume of activation also increased with the addition of the polymers. The role of the desolvation effect by polyelectrolyte of the activated complex was suggested.

Intensive studies have been reported on the catalytic influence of macromolecular substances on various kinds of chemical reactions.[1-3] We ourselves have been engaged in kinetic investigations of interionic reactions in the presence of ionic macromolecules or polyelectrolytes.[4-6] The essential results are that (1) interionic reactions between similarly charged ionic species can be accelerated efficiently by macroions of the opposite charge, (2) reactions between oppositely charged species were retarded by both cationic and anionic macroions, and (3) forward and backward processes are influenced independently by macroions, suggesting that the polyelectrolytes do not fulfil the basic conditions required for catalysts. These results were accounted for in terms of the extended primary salt effect on the basis of the Brönsted–Bjerrum–Manning theory fairly successfully.[6] More recently, we pointed out on the basis of the activation volume data that the stabilization of the activated complex, which gave rise to acceleration, was caused also by dehydration induced by added macroions.[7,8]

In order to make a scrutiny into the true cause of the polyelectrolyte catalysis, it would be highly interesting to study reactions between polyvalent ionic species and the polyelectrolyte influence thereupon. In the present paper, we report data on inorganic reactions between U^{4+} and Tl^{3+} and between $Fe(CN)_6^{4-}$ and $S_2O_8^{2-}$.

Experimental Section

Materials. The aqueous solution of U^{4+} was obtained by electrolytic reduction.[9] Aqueous $Tl(ClO_4)_3$ solution was prepared by dissolving Tl_2O_3 (guaranteed grade) in a $HClO_4$ solution. The concentrations of U^{4+} and Tl^{3+} ions were determined by chelate titration with EDTA, using thorine and xylenolorange as indicators, respectively. $K_4Fe(CN)_6$ and $K_2S_2O_8$ were guaranteed grade reagents commercially available. The concentrations were determined by the gravimetric method and iodometry, respectively.

Sodium poly(ethylene sulfonate) (NaPES) was purchased from Polysciences, Inc. (Warrington, Pa.). The sample was purified by repeated precipitation, using methanol as the precipitant. Then the solution was dialyzed against deionized water. Further purification was carried out by ion exchange through columns of Amberlite IRA-400 and IR-120B.

Polybrene (cationic 3,6-ionenpolymer, 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) was purchased from Aldrich Chemical Co. Milwaukee, Wis. This polymer was purified by repeated precipitation, using acetone as the precipitant. The details of the preparation of poly(4-vinyl-*N*-ethylpyridinium bromide) (C_2PVP) have been described elsewhere.[10] Deionized water obtained with cation- and anion-exchange resins was further distilled for the preparation of solution.

Kinetic Measurements. The reaction rates of U^{4+} with Tl^{3+} were determined from the absorption decrease at 650 nm ascribed to U^{4+}, using a high-sensitivity spectrophotometer (Type SM-401) of the Union Engineering, Hirakata, Osaka-fu. The conversion of the UO_2^{2+} to U^{4+} by the electrolysis was approximately 85%. Further, we could not exclude the contamination of UO_2^{2+} from the reaction solution. However, we note that the presence of UO_2^{2+} does not affect the rate constants, according to Harkness and Halpern.[11] The reaction of $Fe(CN)_6^{4-}$ and $S_2O_8^{2-}$ was followed by the absorption increase at 420 nm ascribed to $Fe(CN)_6^{3-}$, using the above spectrophotometer and a stopped-flow spectrophotometer (Model RA1100, Union Engineering). EDTA was added in the reaction mixture in order to obtain reliable kinetic data, following the procedure of Kershaw and Prue.[12] The details of the apparatuses were described in a previous paper.[13] A high-pressure spectrophotometer (Union Engineering) was used at

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[‡] This work was partly presented at the IUPAC Symposium on Macromolecules, Mainz, 1979.

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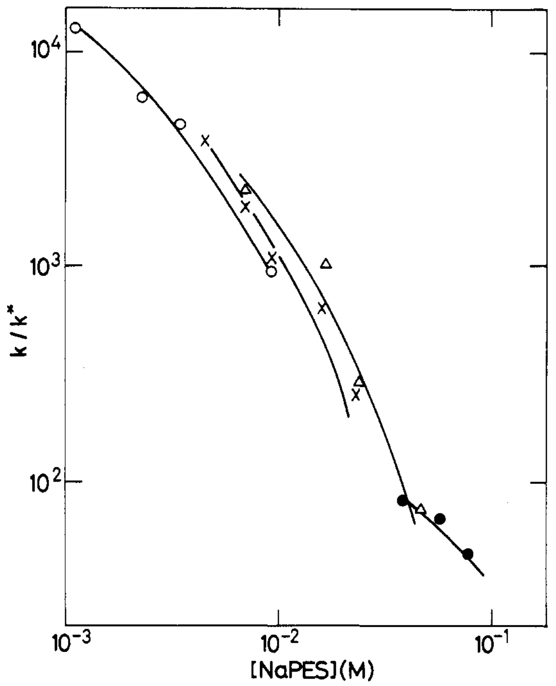
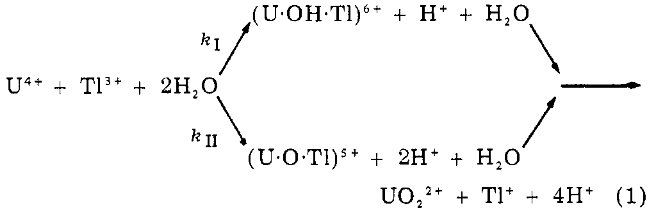


Figure 1. Acceleration factors observed for the U^{4+}–Tl^{3+} reactions with NaPES at 25 °C: (○) $[U^{4+}] = 1.19 \times 10^{-4}$ M, $[Tl^{3+}] = 1.31 \times 10^{-4}$ M, $[H^+] = 0.016$ M; (×) $[U^{4+}] = 1.9 \times 10^{-4}$ M, $[Tl^{3+}] = 1.97 \times 10^{-4}$ M, $[H^+] = 0.03$ M; (△) $[U^{4+}] = 9.28 \times 10^{-4}$ M, $[Tl^{3+}] = 9.86 \times 10^{-4}$ M, $[H^+] = 0.15$ M; (●) $[U^{4+}] = 1.43 \times 10^{-3}$ M, $[Tl^{3+}] = 1.52 \times 10^{-3}$ M, $[H^+] = 0.24$ M

elevated pressure (1–3000 bar). The details of the instrument were also described in the preceding paper.[7]

Results and Discussion

The reaction of U^{4+} and Tl^{3+} is known to proceed via two pathways as is shown in eq 1,[11] where $(U\cdot OH\cdot Tl)^{6+}$ and



$$\begin{tikzcd} & (U\cdot OH\cdot Tl)^{6+} + H^+ + H_2O \arrow[dr] & & \\ U^{4+} + Tl^{3+} + 2H_2O \arrow[ur, "k_I"] \arrow[dr, "k_{II}"'] & & {} \arrow[r] & {} \\ & (U\cdot O\cdot Tl)^{5+} + 2H^+ + H_2O \arrow[ur] & & \end{tikzcd}$$
$$UO_2^{2+} + Tl^+ + 4H^+ \quad (1)$$

$(U\cdot O\cdot Tl)^{5+}$ are the activated complexes. The overall second-order rate constants, k, are shown as a function of the concentration of sodium poly(ethylene sulfonate) (NaPES) in Figure 1, where k^* is the rate constant without the macroions. In order to observe large acceleration factors by the macroions, we carried out the experiments at relatively low concentrations of $HClO_4$. The fraction of the hydrolysis product of U^{4+}, i.e., UOH^{3+}, was below 10% under the experimental conditions according to the UV measurements.[14] At low H^+ concentrations, k^* is expected to be large as was observed earlier.[11] This tendency is also understood from eq 2 to be described below. The largest acceleration factor was about 10^4 at $[NaPES] \simeq 10^{-3}$ M, and the factor decreased with increasing polymer concentration. The kinetic study at lower concentrations was difficult because precipitation developed.

The temperature dependence of the rates of the U^{4+}–Tl^{3+} reaction is shown in Figure 2. Excellent linearity was obtained between log k and $1/T$, both in the presence of NaPES and in its absence. The thermodynamic parameters of the reaction are compiled in Table I. The literature values of $\Delta S^{\ddagger}$ were 46 and 50 J mol^{-1} K^{-1} when the H^+ concentrations are 1 and 2 M, respectively.[11] The reason for the disagreement between the reported values and ours (−8 J mol^{-1} K^{-1}) is not clear. However, it may be due to the striking differences in the ionic strength and the proton concentration, as will be mentioned below. It is seen that the polyelectrolyte catalysis is due to an increase in $\Delta S^{\ddagger}$. For the interionic reaction between similarly charged species in the absence of macroions, the volume of activation, $\Delta V^{\ddagger}$, is expected to be negative, if the solvation factor plays a primary role.[15] However, the observed value was positive, i.e., $\Delta V^{\ddagger} = +8.0$ mL mol^{-1} at $[H^+] = 1.53$ M. We note that our measurements were carried out at a very high concentration of $HClO_4$ (1.53 M). At such high concentrations, the simple electrolyte ions would desolvate the reactant ions and even more strongly the activated complex (having higher valency than the reactant ions). This desolvation would give positive $\Delta V^{\ddagger}$ for the present case. It should be noted that the disagreement of the reported $\Delta S^{\ddagger}$ values and ours mentioned above would also be explainable by this desolvation effect. The increase of $\Delta V^{\ddagger}$ caused by NaPES addition is notable, which will probably be consistent with the $\Delta S^{\ddagger}$ increase, reflecting the dehydration of the activated complex by the macroions. The important contribution of the dehydration effect of macroions for the other interionic reactions was discussed in the previous papers in detail.[7,8]

We then determined the rate constants k_I and k_{II} from the $[H^+]$ dependence of the k values by

$$k = k_I/[H^+] + k_{II}/[H^+]^2 \quad (2)$$

We carried out the $k[H^+]^2$ vs. $[H^+]$ plots and obtained k_I and k_{II} from the slope and intercept of the linear relation. The plots are shown in Figures 3 and 4 for the reactions in the absence of NaPES and in its presence, respectively. The linearity was satisfactory under the experimental conditions employed. The k_I and k_{II} thus obtained are shown in Table II. The results were sensitive to the proton concentrations where the $k[H^+]^2$ vs. $[H^+]$

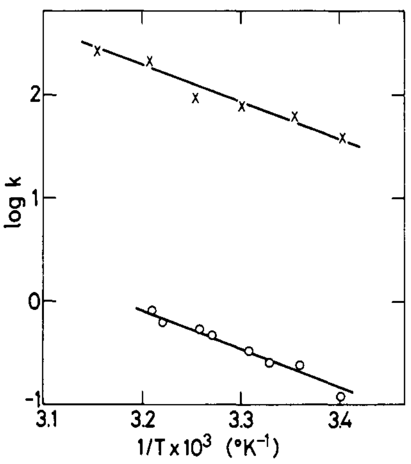


Figure 2. Temperature dependence of the k values of the U^{4+}–Tl^{3+} reaction: $[U^{4+}] = 7.75 \times 10^{-4}$ M, $[Tl^{3+}] = 9.33 \times 10^{-4}$ M, $[H^+] = 0.115$ M; (○) [NaPES] = 0 M; (×) 2.34×10^{-2} M.

Table I
Thermodynamic Parameters of the U^{4+}–Tl^{3+} Reaction

	k/k^{*a}	$\Delta G^{\ddagger}$,[a] kJ mol^{-1}	$\Delta H^{\ddagger}$,[a] kJ mol^{-1}	$\Delta S^{\ddagger}$,[a] J mol^{-1} K^{-1}	$\Delta V^{\ddagger}$,[b] mL mol^{-1}
none	1	77.0 ± 0.3	74.1 ± 2	−8 ± 6	8.0 ± 2
NaPES	70	63.2	73.6	38	21

[a] $[U^{4+}] = 7.75 \times 10^{-4}$ M; $[Tl^{3+}] = 9.33 \times 10^{-4}$ M; $[H^+] = 0.115$ M; [NaPES] = 2.34×10^{-2} M; 31 °C.
[b] $[U^{4+}] = 1.12 \times 10^{-3}$ M; $[Tl^{3+}] = 3.06 \times 10^{-3}$ M; $[H^+] = 1.53$ M; [NaPES] = 0.151 M; 25 °C.

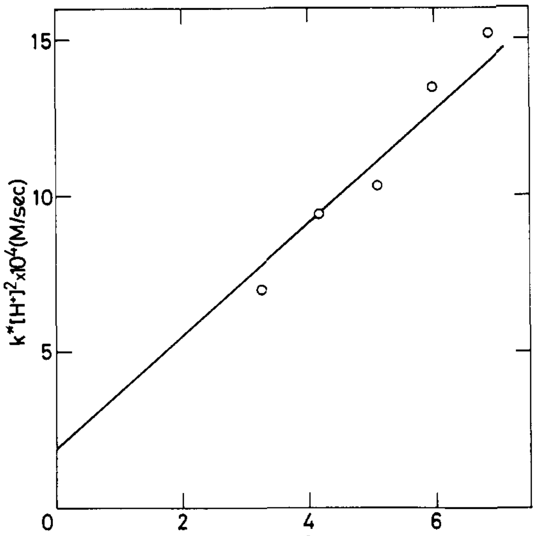


Figure 3. $k^*[H^+]^2$ vs. $[H^+]$ plots for the U^{4+}–Tl^3 reaction at 25 °C: $[U^{4+}] = 2 \times 10^{-4}$ M, $[Tl^{3+}] = 2.2 \times 10^{-4}$ M, $[H^+] = 3.27 \times 10^{-2}$–$6.87 \times 10^{-2}$ M

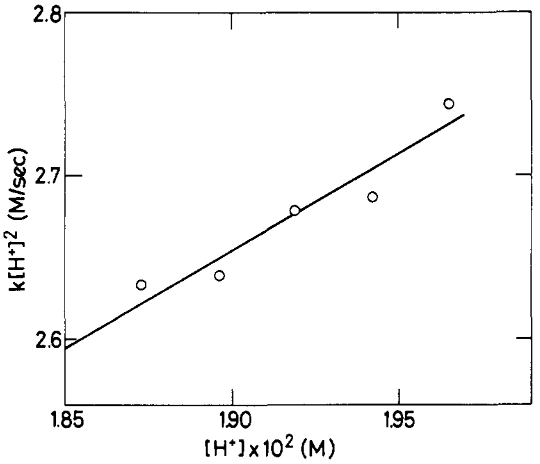


Figure 4. $k[H^+]^2$ vs. $[H^+]$ plots for the U^{4+}–Tl^{3+} reaction in the presence of NaPES at 25 °C.: $[U^{4+}] = 2 \times 10^{-4}$ M, $[Tl^{3+}] = 2.2 \times 10^{-4}$ M, [NaPES] = 1.5×10^{-3} M, $[H^+] = 1.87 \times 10^{-2}$–$1.97 \times 10^{-2}$ M.

Table II
Acceleration Factors of the Two Pathways of the U^{4+}-Tl^{3+} Reactions at 25 °C[a]

	[NaPES], M		acceleration factor
	0	1.15×10^{-3}	
k_I, s^{-1}	0.0181	119	$k_I/k_I^* = 6600$
k_{II}, Ms^{-1}	1.92×10^{-4}	0.387	$k_{II}/k_{II}^* = 2000$

[a] $[U^{4+}] = 2 \times 10^{-4}$ M; $[Tl^{3+}] = 2.2 \times 10^{-4}$ M; $[H^+] = 1.87 \times 10^{-2}$–$6.87 \times 10^{-2}$ M.

plots were carried out, and the agreement between the literature values[11] and ours was not always satisfactory; the k_I and k_{II} values observed in this work were smaller than the literature values and particularly so for the k_{II}. This would be explained by the fact that this interionic reaction proceeds between similarly charged ionic species and the rate constant increases with increasing ionic strength ($HClO_4$ concentration in the present case) by the primary salt effect.[16] As was mentioned before, our experiments were carried out at low concentrations of $HClO_4$. Thus, the smaller values of k_I and k_{II} obtained by us would be reasonable. Evidently, k_I was seen to increase by polyelectrolyte addition to a greater extent than k_{II}. This can be easily accepted if we apply the Brönsted–Bjerrum equation of the primary salt effect, which reads for the respective pathway,

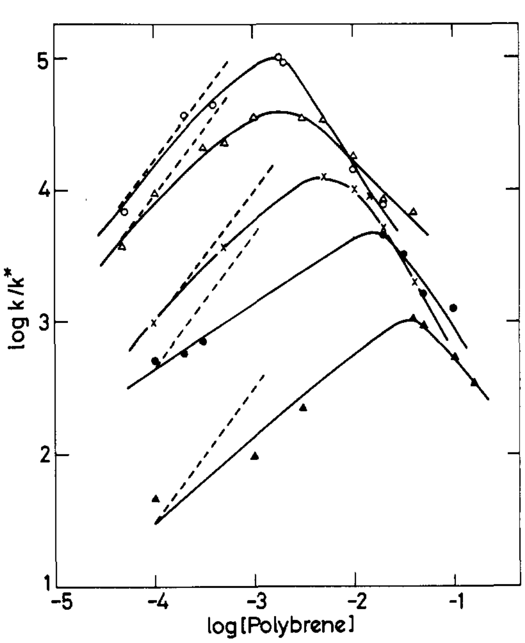


Figure 5. Acceleration factors observed for the $Fe(CN)_6^{4-}$–$S_2O_8^{2-}$ reaction with polybrene at 25 °C: (○) $[K_4Fe(CN)_6] = 2.17 \times 10^{-5}$ M, $[K_2S_2O_8] = 6 \times 10^{-4}$ M, [EDTA] = 10^{-5} M; (△) $[K_4Fe(CN)_6] = 3.25 \times 10^{-5}$ M, $[K_2S_2O_8] = 9 \times 10^{-4}$ M; (×) $[K_4Fe(CN)_6] = 6.50 \times 10^{-5}$ M, $[K_2S_2O_8] = 1.8 \times 10^{-3}$ M; (●) $[K_4Fe(CN)_6] = 1.3 \times 10^{-4}$ M, $[K_2S_2O_8] = 3.6 \times 10^{-3}$ M; (▲) $[K_4Fe(CN)_6] = 3.25 \times 10^{-4}$ M, $[K_2S_2O_8] = 9 \times 10^{-3}$ M.

$$k_I/k_I^* = f_{U^{4+}} f_{Tl^{3+}} / f_{(U\cdot OH\cdot Tl)^{6+}} \quad (3)$$

$$k_{II}/k_{II}^* = f_{U^{4+}} f_{Tl^{3+}} / f_{(U\cdot O\cdot Tl)^{5+}} \quad (4)$$

where f denotes the activity coefficient. The numerators of the right-hand side of eq 3 and 4 are identical, so that the observed fact ($k_I/k_I^* > k_{II}/k_{II}^*$) requires $f_{(U\cdot OH\cdot Tl)^{6+}}$ to be smaller than $f_{(U\cdot O\cdot Tl)^{5+}}$ in the presence of the macroions. This relative magnitude of the f is entirely reasonable in light of numerous existing data of the activity coefficient in dilute polyelectrolyte solutions, because the interaction of the macroions with hexavalent species should be stronger than that with pentavalent ones. In other words, the hexavalent activated complex was more strongly stabilized than the pentavalent one, so that the polyelectrolyte acceleration of the k_I process was more distinct. This indicates that the stabilization of the activated complex is highly important in polyelectrolyte catalysis.

It should be remembered that the present results cannot be accounted for in terms of the so-called concentration effect of reactant as such, if this effect is taken to imply that the reactant accumulation results in enhanced collision and rate enhancement. If this explanation is correct, we should observe the identical acceleration for the two pathways, because the reactants are the same for the two pathways.

The acceleration factor k/k^* for the $Fe(CN)_6^{4-}$–$S_2O_8^{2-}$ reaction in the presence of polybrene is shown in Figure 5. The value increased with increasing concentration of the macroions and decreased after passing through a maximum. The polymer concentration at which the maximum was observed increased with increasing reactant concentration. The mechanism of the reaction between potassium ferrocyanide and potassium peroxydisulfate was studied by Chlebek and Lister[17] in detail. They proposed that the true rate-determining step was the reaction between $KFe(CN)_6^{3-}$ and $KS_2O_8^-$ and not that between Fe-

Table III
Thermodynamic Parameters of the $Fe(CN)_6{}^{4-}$-$S_2O_8{}^{2-}$ Reactions

polyelectrolyte	[polyelectrolyte]	k/k^*	$\Delta G^{\ddagger}$,[c] kJ mol^{-1}	$\Delta H^{\ddagger}$,[c] kJ mol^{-1}	$\Delta S^{\ddagger}$,[c] J mol^{-1} K^{-1}	$\Delta V^{\ddagger}$,[d] mL mol^{-1}
none[a]	0	1	8.54 ± 0.3	33.9 ± 2	−167 ± 8	10 ± 2
polybrene[a]	0.0872	290	72.8	26.8	−146	16
C_2PVP[b]	5.94×10^{-3}	18000	63.2	26.4	−121	

[a] $[Fe(CN)_6{}^{4-}] = 6.5 \times 10^{-4}$ M; $[S_2O_8{}^{2-}] = 0.018$ M; [EDTA] = 10^{-4} M. [b] $[Fe(CN)_6{}^{4-}] = 3.25 \times 10^{-5}$ M; $[S_2O_8{}^{2-}] = 9 \times 10^{-4}$ M; [EDTA] = 10^{-5} M. [c] 30 °C. [d] $[Fe(CN)_6{}^{4-}] = 6.5 \times 10^{-4}$ M; $[S_2O_8{}^{2-}] = 0.018$ M; [EDTA] = 10^{-4} M; 25 °C.

$(CN)_6{}^{4-}$ and $S_2O_8{}^{2-}$. If we accept this mechanism, in other words, if the reaction proceeds between the trivalent anions and the monovalent anions, the acceleration factor catalyzed by polymer is given by the Brönsted-Bjerrum-Manning theory as follows[18]

$$\ln (k/k^*) = \ln (X_A/X_A{}^*) - \frac{1}{18\xi}\left[\frac{1}{\xi^{-1} - 2 + \dfrac{12}{X_A} + \dfrac{2}{X_B} + \dfrac{2}{X_S}} - \frac{1}{\xi^{-1} - 2 + \dfrac{12}{X_A{}^*} + \dfrac{2}{X_B{}^*} + \dfrac{2}{X_S{}^*}}\right] \quad (5)$$

where $X_A = m_2/m_A$, $X_B = m_2/m_B$, and $X_S = m_2/m_S$, ξ is the charge density parameter of the Manning theory, m_A and m_B denote the molar concentrations of the reactants, respectively, m_2 is the concentration of the polyelectrolyte, and the asterisk indicates the absence of the macroions. The second term of the right-hand side of eq 5 is negligibly small compared with the first one. Thus, we obtain the following simple equation,

$$k/k^* = X_A/X_A{}^* \quad (6)$$

The broken lines in Figure 5 are the calculated values of k/k^* using eq 6. Agreement between the observed and the calculated values is gratifying at low concentrations of reactant ions and macroions. The influence of foreign salt, i.e., potassium chloride, on the acceleration factor is seen in Figure 6. The acceleration was decreased by the addition of the salt. The broken lines are also calculated from eq 6. The acceleration effect of poly(4-vinyl-N-ethylpyridinium bromide) (C_2PVP) is shown in Figure 7. A situation obtained for polybrene was also observed for the present polymer. In this case, comparison of the Brönsted-Bjerrum-Manning theory with experiments was difficult, because the reliable data were not obtained in the dilute concentration region of the polymer, i.e., 10^{-5}-10^{-3} M.

From the agreement obtained between the experiment and theory, we cannot exclude the important contribution of the electrostatic stabilization effect. However, we should note that, for reactions between similarly charged ionic species, the Brönsted-Bjerrum-Manning theory cannot predict the magnitude of the acceleration factor, but it gives its dependence on polymer concentration only.[6] Therefore, it is impossible to estimate the electrostatic stabilization effect in a quantitative manner from the theory, as far as the reactions under consideration are concerned.

The thermodynamic parameters of the $K_4Fe(CN)_6$-$K_2S_2O_8$ reaction are given in Table III. The ΔS^{*} value in the absence of polymer obtained by us was smaller than the reported value,[17] i.e., $\Delta S^{*} \simeq -84$ J mol^{-1} K^{-1}.[4] It should be noted that the literature value is not as reliable because it was obtained by using the k values at two different temperatures only, i.e., 25 and 40 °C. It is seen that the polyelectrolyte catalysis is due to an increase in ΔS^{*} and a decrease in ΔH^{*}, both causing the lowering of the free energy of the activated complex. The observed ΔV^{*} value in the absence of macroions was positive, which is in disagreement with the prediction by Laidler and Bunting[15] as is discussed above. The clear-cut reason is not clear. However, we should remember the specific cation effect

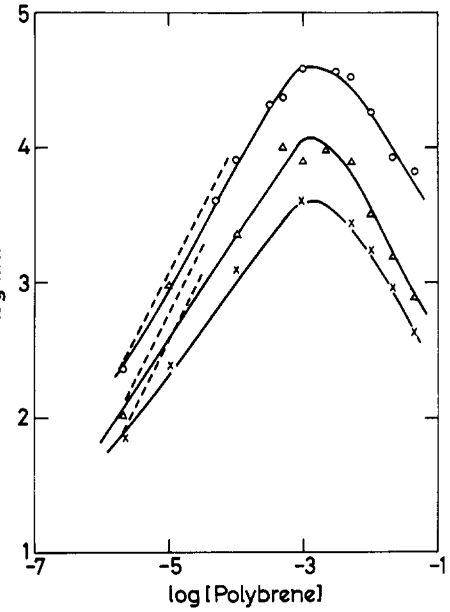


Figure 6. Acceleration factors observed for the $Fe(CN)_6{}^{4-}$-$S_2O_8{}^{2-}$ reactions with polybrene at 25 °C: $[K_4Fe(CN)_6] = 3.25 \times 10^{-5}$ M, $[K_2S_2O_8] = 9 \times 10^{-4}$ M, [EDTA] = 10^{-5} M; (○) [KCl] = 0 M, (△) 0.001 M, (×) 0.01 M.

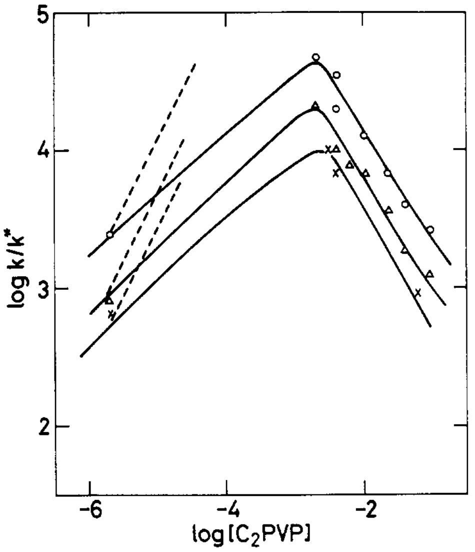


Figure 7. Acceleration factors observed for the $Fe(CN)_6{}^{4-}$-$S_2O_8{}^{2-}$ reactions with C_2PVP at 25 °C: $[K_4Fe(CN)_6] = 3.25 \times 10^{-5}$ M, $[K_2S_2O_8] = 9 \times 10^{-4}$ M, [EDTA] = 10^{-5} M; (○) [KCl] = 0 M, (△) 0.001 M, (×) 0.01 M.

for this reaction found by Kershaw and Prue,[12] i.e., a cation is incorporated into the activated complex. The increase of the size of the activated complex by the introduced cation might have some bearing on the positive activation volume. The volume of the activation, $\Delta V^{\ddagger}$, was increased by the addition of macroions, similar to the increase observed for the U^{4+}–Tl^{3+} reaction. This increase of $\Delta V^{\ddagger}$ again shows the important contribution of the "dehydration effect" of the activated complex by the macroions, if the specific cation effect remains unaffected by the presence of the macroions.

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Role of Solvent in Polymer "Catalysis". Polyelectrolyte Catalysis on the Esterolysis of Neutral and Ionic Esters in Hexanol–Water Mixtures

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ABSTRACT: The catalytic activities of three kinds of poly(ethylenimines) quaternized with *n*-octyl bromide, *n*-lauryl bromide, and *n*-cetyl bromide (C8PEI, C12PEI, and C16PEI) on the alkaline hydrolysis of *p*-nitrophenyl acetate (PNPA), 3-nitro-4-acetoxybenzoic acid (NABA), and 3-acetoxy-*N*-(trimethylanilinium) iodide (ANTI) were studied in 1-hexanol–water mixtures. The reactivity of OH^- was found to be enhanced in the mixtures with decreasing water content. Furthermore, the remarkable role of the solvation effect of the polymers was shown; the polymers absorbed water molecules strongly and selectively from the mixture of 1-hexanol–water. These solvation and desolvation effects were also studied by fluorescence and light-scattering measurements.

The gigantic rate enhancement and retardation effects of macroions on chemical reactions, in particular on interionic reactions, were intensively investigated,[1–5] and the main cause for the catalysis was ascribed to strong electrostatic and hydrophobic interactions between the reactant species and the macroions.

For comparatively simple reaction systems, the theoretical interpretation by the Brönsted–Bjerrum–Manning theory was fairly successful, suggesting that electrostatic stabilization of the activated complex is responsible for the acceleration and that of the reactant is a cause of the deceleration.[6–8]

Recent studies of high-pressure influence of the polyelectrolyte catalysis revealed that the solvation and desolvation effects of reactant ions and/or activated complex are playing a key role in addition to the electrostatic stabilization mentioned above.[9] These solvent effects in polymer "catalysis" are certainly expected to manifest themselves clearly for reactions in organic solvents. Some studies have been reported on catalytic influences of polymers in organic solvent–water mixtures.[10–18] However, the hydration or dehydration effects of polymers were not investigated in detail. In organic solvents, ions are often reported to be dehydrated.[19,20] Furthermore, recent studies of catalytic effects of reversed micelles and liquid crystals have clearly demonstrated the important role of solvent molecules.[21–23]

Thus it was thought interesting to examine the catalytic action of polyelectrolytes in organic solvents. In the present paper, we studied the influence of polyelectrolytes on the alkaline hydrolysis of various esters in 1-hexanol containing small amounts of water.

Experimental Section

Materials. Poly(*N*-octylethylenimine bromide) (C8PEI), poly(*N*-laurylethylenimine bromide) (C12PEI), and poly(*N*-cetylethylenimine bromide) (C16PEI) were prepared by quaternization of poly(ethylenimine) with octyl bromide, lauryl bromide, and cetyl bromide, respectively. The poly(ethylenimine) was donated from Nippon Shokubai Co., Tokyo, and its degree of polymerization was 100. The quaternization was carried out in a nitromethane and nitroethane mixture (1:1) at 50 °C for 4 days. The degrees of quaternization of C8PEI, C12PEI, and C16PEI were 55, 58, and 59%, with respect to the total amount of nitrogen atoms in the polymer, respectively. The purification was carried out by reprecipitation with ethyl acetate. These polymers were soluble in 1-hexanol but insoluble in water. Cetyltrimethylammonium bromide (CTABr) and Brij35 $[C_{12}H_{25}(OCH_2CH_2)_{23}\text{-}OH]$ were commercially available and were used without further purification.

p-Nitrophenyl acetate (PNPA) was commercially available and further purified twice by crystallization from chloroform. 3-Acetoxy-*N*-(trimethylanilinium) iodide (ANTI) was synthesized by the method of Overberger et al.[24] and was purified by recrystallization in nitromethane. 3-Nitro-4-acetoxybenzoic acid (NABA) was prepared by the method of Overberger et al.[25] and was crystallized from benzene.

8-Anilino-1-naphthalenesulfonic acid ammonium salt (ANS) was purchased from the Wako Pure Chemical Co., Osaka, and purified by repeated crystallization from water.

1-Hexanol was of a spectral grade and was further distilled before use. For solution preparation, water was deionized and then distilled.

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